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(21) International Application Number: PCT/FI98/00480 (22) International Filing Date: 3 June 1998 (03.06.98) (30) Priority Data: 972381 5 June 1997 (05.06.97) FI (71) Applicant (for all designated States except US): NESTE OY [FI/FI]; Keilaniemi, FIN-02150 Espoo (FI). (72) Inventors; and (75) Inventors/Applicants (for US only): PRIMACHENKO, Oleg Nikolaevich [RU/RU]; Suzdalsky pr., 67-13, St.Petersburg, 195276 (RU). FAVLYUCHENKO, Valery, N. [RU/RU]; Energetikov pr., 66-1-205, St.Petersburg, 195253 (RU). GAGARINA, Klavdia, A. [RU/RU]; Mechnikov pr., 17-79, St.Petersburg, 195271 (RU). IVANCHEV, Sergey Stepanovich [RU/RU]; ul. Nalichnaya, 36-3-97, St.Petersburg, 199226 (RU). SKRIFVARIS, Mikael [FI/FI]; Katajahaantie 2 A 20, FIN-00200 Helsinki (FI). LAA-MANEN, Hanna [FI/FI]; Kaivomestarinkatu 3 D 56, FIN-00200 Helsinki (FI). KOSKINEN, Jukka [FI/FI]; Westendintie 105, FIN-02160 Espoo (FI). (74) Agent: FORSSÉN & SALOMAA OY; Yrjönkatu 30, FIN-00100 Helsinki (FI).		(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, GM, GW, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG). Published <i>With international search report.</i>
(54) Title: METHOD FOR THE PREPARATION OF COPOLYMERS FOR ANTISTATIC POLYMERIC COATINGS		
(57) Abstract <p>The invention is related to a method for the preparation of copolymers by latex copolymerization for antistatic polymeric coatings, comprising a process for the manufacture of antistatic copolymer latexes based on vinyl aromatic compounds, alkyl esters of methacrylic acid or acrylic acid and amine alkyl esters of methacrylic acid and/or vinyl pyridine derivatives wherein the latexes of the above copolymers are prepared by emulsion copolymerization in the presence of trimethyl alkyl ammonium halogenide in the amount of 2-4 % of the total weight of the monomers in combination with a water soluble initiator, wherein the formation of latex particles with the direct morphology of core-shell takes place, the core comprising the copolymer formed in stage 1 of the process and the shell comprising the copolymer formed in stage 2 of the process.</p>		

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Method for the Preparation of Copolymers for Antistatic Polymeric Coatings

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The present invention is related to a method for the preparation of copolymers by latex copolymerization for antistatic polymeric coatings.

These copolymers can be used as antistatic and electric dissipative materials, as
10 coatings in pulp and paper industry, in ship building industry, in electronic industry and also for the manufacture of photographic materials and instruments.

In the prior art there are available some methods to prepare the said copolymers. One of the known approaches to manufacture polymeric materials with long-term
15 antistatic effects is the preparation of copolymers containing ionizable functional groups, which impart stable antistatic properties to the materials based on such copolymers. Toxic reagents and organic solvents, which in many cases are also flammable, are often used in these processes.

20 The patent publication CN 1084200 describes the preparation and use of antistatic coatings based on polymeric compounds in the latex form, and specially some styrene-acrylate latex compounds with low molecular antistatic agents, fillers and pigments are disclosed. The latex copolymers of this publication are used as binders for antistatic agents, fillers and pigments.

25

Low molecular antistatic agents are not able to provide coatings with a stable long-term antistatic effect due to the antistatic diffusion from the surface of the coating. Another disadvantage of the disclosed latex compounds is the fact that when various ingredients are added to the latex, problems appear with the aggregative stability of
30 the latex compound and its long-term storage stability, when segregation and separation tend to occur.

In the patent publication EP 338 486 is disclosed a process for the production of stable emulsion polymers with inverted core-shell latex particle structure suitable for the production of functionalized latexes. At the first stage of the process low molecular hydrophilic copolymer in latex form is formed. At this stage it is possible
5 to produce amine and carboxy containing latexes. During a later stage of the process the hydrophobic core of the latex particle is formed in the presence of the hydrophilic copolymer latex. This process requires the use of 0.5—6% of chain transfer agent, and water soluble initiators of persulphate type to obtain low molecular hydrophilic copolymer. As it is commonly known, the use of bromine containing
10 compounds as chain transfer agents in such high concentrations as described in this publication may result in undesirable colouring of the coatings and thus it limits the applications of these latexes.

Further there appears no teaching in this publication concerning the possible antistatic
15 properties of the coatings based on the latexes obtained and further, no information is available about the distribution of the functionalized copolymer in the core-shell latex particle.

The distribution is a very important parameter for the formation of latex coatings with antistatic properties, in this process the functionalized copolymer is concentrated on the surface of the latex particle.
20

Further, the use of cationic surfactants which can impart an additional antistatic effect to latex coatings due to their structure, when surfactants are located on the
25 surface of the latex particle, is not disclosed in the said publication.

An object of the present invention lies in providing a method for the preparation of stable copolymers for antistatic latex coatings characterized by high water resistance and good adhesion to various supports.
30

A further object lies in developing of processes for the production of copolymer latexes for antistatic polymeric coatings with improved antistatic properties and higher water resistance.

- 5 A further object lies in providing a method for the manufacture of concentrated latexes with solid content exceeding 40 % and with low viscosity.

The process according to the invention for the manufacture of antistatic copolymer latexes based on vinyl aromatic compounds, alkyl esters of methacrylic acid or
10 acrylic acid and aminealkyl esters of methacrylic acid and/or vinylpyridine derivatives is characterized in that the latexes of the above copolymers are prepared by emulsion copolymerization in the presence of trimethylalkylammonium halogenide in the amount of 2—4% of the total weight of the monomers in combination with a water soluble initiator, wherein the formation of latex particles with the direct
15 morphology of core-shell takes place, the core consisting of the copolymer formed in stage 1 of the process and the shell consisting of the copolymer formed in stage 2 of the process.

Surprisingly the inventors of the present invention have been able to develop
20 methods for the production of amine containing copolymers of core-shell type in the form of aqueous latexes with the aid of two stage core-shell emulsion copolymerization in the presence of cationic surfactants in combination with water soluble azo compounds. These methods for the preparation of latex copolymers for antistatic coatings are actually processes for the production of functionalized latexes. The shell
25 of the latex particle contains copolymers with ionizable functional groups, which impart stable antistatic properties to the coatings based on such copolymers. Amine and ammonium groups can be used as such functional groups of the copolymer.

According to the invention a trimethylammonium halogenide is used as cationic
30 surfactant. The alkyl group is selected from cetyl, dodecyl and stearyl groups. The preferable surfactant is dodecyltrimethylammonium halogenide.

Cationic surfactants may act as antistatics, and here cationic surfactants such as trimethylalkylammonium halides are used as emulgators which provide aggregative stable amine containing latexes. The functional groups of said cationic surfactants are compatible with the functionalized copolymers being synthesized, i.e. amine containing styrene-acrylate copolymers containing tertiary amine groups responsible for the antistatic properties. Therefore these surfactants can be expected to strengthen the antistatic effect since the primary zone of surfactant localization is the surface of latex particles.

10 The seed latexes of copolymers, which form the cores of the latex particle are produced at the first stage of the process. The seed latexes are based on vinyl aromatic compounds, alkyl esters of methacrylic acid or acrylic acid. Dimethacrylic ester of ethyleneglycol is used as a cross-linking agent with the weight ratio of monomers equal to 20—80:79—19.9:1.0—0.1, preferably 40—60:59.8—39.6:0.2—0.4 in the case of single feeding of the monomeric mixture to the emulsifier solution. The second stage of the process is the formation of the amine containing shell of the latex particle. The final stage is carried out stepwise with feeding of the monomeric mixture of vinyl aromatic compound, alkyl ester of methacrylic acid or acrylic acid, aminealkyl ester of methacrylic acid and/or vinylpyridine derivative with the weight ratio of monomers equal to 25—50:65—15:10—35, preferably 33—40:53—22:14—28 or alternatively with feeding of vinylaromatic compound, alkylester of methacrylic acid or acrylic acid, aminealkyl ester of methacrylic acid and/or vinylpyridine derivative, dimethacrylic ester of ethyleneglycol as a cross-linking agent with the weight ratio of monomers equal to 25—50:64—14.9:10—35:0.1—0.1, preferably 36.3—51.6:54—34:9.5:14:0.2—0.4.

At the first stage of the process, at the seed copolymerization the amounts of vinylaromatic compound and alkyl esters of methacrylic acid or acrylic acid can be varied within the range of 20—75 % calculated from the total amount of the monomers, and preferably within the range of 25—50 %.

Styrene and alkyl or halogen substituted derivatives of styrene can be used as vinyl-aromatic compounds, preferably styrene and p-methylstyrene are used.

5 Methyl, ethyl, butyl, octyl or 2-ethylhexyl acrylates and methyl, ethyl or butyl methacrylates can be used as alkyl esters of methacrylic acid or acrylic acid and preferably methyl and butyl acrylate and butyl methacrylate are used.

Dimethyl and diethylamineethyl methacrylates can be used as aminealkyl esters of methacrylic acid.

10

Vinylpyridine, 2-methyl-5-vinylpyridine, 5-ethyl-2-vinylpyridine, 1,2-dimethyl-5-vinylpyridinylmethyl sulphate can be used as derivatives of vinylpyridine, preferably 2-methyl-5-vinylpyridine is used.

15 The ratio of monomers and water in the manufacturing process of latexes can vary from 1:1 to 1:4, preferably the ratio 1:1 to 1:2 is used.

The latex copolymerization reaction is carried out at the temperature range of 65—85 °C, preferably at 70—80 °C.

20

The latexes are polymerized at pH of the reaction equal to 1—8, and acidifying reagents, in particular hydrochloric acid may optionally be used.

25 When vinylpyridine derivatives are used as amine monomers, aggregative stable latexes are prepared in both acidic, neutral and weakly alkaline fluids. When amine alkyl esters of methacrylic acid (DMAEMA and DEAEMA) are used as amine monomers, aggregative stable latexes are prepared only in acidic conditions, and in this case it is necessary to use hydrochloric acid.

30 Further, the addition of hydrochloric acid is also necessary for the transformation of the functional groups of amine monomers into salt form, and it improves the antistatic properties of coatings based on such copolymers.

Optionally initiators such as cumene hydroperoxide, β -oxyethyl-tert-butyl peroxide, β -oxypropyl-tert-butyl peroxide and 2,2'-azo-bis-(2-aminepropane) dihydrochloride can be used, as well as chain transfer agents such as tert-dodecyl mercaptane, inorganic pigments such as titanium dioxide and coalescent additives such as monoethyl ester of ethyleneglycol (ethyl cellosolve) can be applied.

The functionalized, aggregative, stable latexes manufactured using the above disclosed methods, for antistatic coating and other applications, exhibit an optimum combination of antistatic and mechanical properties with ρ_s in the range equal to $1 \times 10^5 - 2 \times 10^{10}$ ohm at relative humidity of 65—32 %. These latexes are also well suited for coloured applications. The film forming temperature can be reduced if additional coalescent additives are used. The functionalized latexes manufactured according to the present method are suitable for the concentrated stable latexes with approximately 50 % or more solids due to the increased particle size of the latex particle formed, due to lower surface energy of the system and due to lower viscosity of the latex.

The advantages of the preparation of latex coatings from aqueous latexes compared to coatings based on organic solvents are evident because these materials are non-toxic and non-inflammable, and additionally no transfer agents are needed in the process. The said copolymer latexes exhibit improved antistatic properties and yield latex coatings with increased water resistance.

The following examples are illustrative embodiments of the present invention and are not meant to narrow the scope of the process of the invention. Additionally two comparative examples based on the process described in EP 338 484 are provided in order to illustrate the advantages of the present invention.

The properties of latexes and polymeric coatings obtained in examples 1—15 and comparative examples 16—17 are presented in tabulated form on pages 18—19.

Example 1.**Seed polymerization, stage 1:**

5 200 g deionized water is charged into a 500 ml reactor equipped with a reflux condenser, a stirrer, a dropping funnel, a thermometer and an inlet tube for inert gas. The agitation is started, 2.0 g (2 % of the total weight of monomers) trimethyl dodecyl ammonium chloride (TMDDAC) as a cationic emulsifier is charged, the reaction mixture is purged with inert gas (nitrogen/argon), the content of the reactor
10 is heated to 70 °C, the monomer mixture consisting of 10.0 g (10% w/w) styrene (ST), 14.95 g (14.95 % w/w) butyl acrylate (BA), 0.05 g (0.05 % w/w) dimethacrylic ester of ethylene glycol (DMEG), which amounts to 25 % of the total weight of comonomers, is charged, 0.1 g (0.1 % w/w) water soluble azo initiator 2,2'-azo-bis-(2-amine propane) dihydrochloride and the stage of seed copolymerization is carried
15 out at 70 °C for 1 h.

Copolymerization, stage 2:

When the seed polymerization is completed, 0.1 g (0.1 % w/w) of the azo initiator,
20 0.5 ml 35 % aqueous solution of hydrochloric acid are charged, and the feeding of the monomer mixture consisting of 27.2 g (27.2 % w/w) ST, 40.65 g (40.65 % w/w) BA, 7.0 g (7 % w/w) diethyl amine ethyl methacrylate (DEAEMA), 0.15 g (0.15 % w/w) DMEG, which amounts to 75 % of the total weight of monomers, is started and continued for 4 h with the rate of 18.75 g/hr. 2 h after the beginning of the of
25 copolymerization stage 0.1 g (0.1 % w/w) of the azo initiator is charged. When the feeding of the monomer mixture is completed the last portion of the azo initiator 0.1 g (0.1 % w/w) is charged and the reaction mixture is kept at 70 °C for 0.5 h. Then the temperature is raised to 75 °C and the latex is heated at this temperature for 1 h. The latex is cooled and collected. In the synthesis of latex the mono-
30 mer/water ratio is 1:2.

Example 2

A procedure according to example 1 was performed with the following amounts of starting materials:

5	Seed polymerization:	2 g (2 % w/w) TMDDAC
	Stage 1	30.0 g (30.0 % w/w) ST
		19.8 g (19.8 % w/w) BA
		0.2 g (0.2 % w/w) DMEG (50% of the total weight of
10		monomers)
		0.125 g (0.125 % w/w) azo initiator
	Copolymerization:	0.125 g (0.125 % w/w) azo initiator
	Stage 2	25.58 g (25.58 % w/w) ST
		17.12 g (17.12 % w/w) BA
15		7.0 g (7.0 % w/w) DEAEMA
		0.2 g (0.2 % w/w) DMEG (50% of the total weight of
		monomers)
		0.125 g (0.125 % w/w) azo initiator (added in 2 h after
		beginning of stage 2)
20		0.125 g (0.125 % w/w) azo initiator (added after the
		feeding of monomers of stage 2 is finished)
	Monomer feeding rate:	12.5 g/h
	Monomer/water ratio:	1:2

Example 3

A procedure according to example 1 was performed with the following amounts of starting materials:

30	Seed polymerization:	2.0 (2 % w/w) TMDDAC
	Stage 1	16.61 g (16.61 % w/w) ST
		16.61 g (16.61 % w/w) BA

0.067 g (0.067 % w/w) DMEG (33.3% of the total weight of the monomers)
0.167 g (0.167 % w/w) azo initiator
Copolymerization: 0.167 g (0.167 % w/w) azo initiator
5 Stage 2 29.79 g (29.79 % w/w) ST
29.78 g (29.78 % w/w) BA
7.0 g (7 % w/w) 2-M-5-VP (2-methyl-5 vinyl pyridine)
0.133 g (0.133 % w/w) DMEG (66.7% of the total weight of monomers)
10 0.167 g (0.167 % w/w) azo initiator (added in 2 h after the beginning of stage 2)
Monomer feeding rate: 16,68 g/h
Monomer/water ratio: 1:2

15 Example 4

A procedure according to example 1 was performed with the following amounts of starting materials:

20 Seed polymerization: 2.0 g (2 % w/w) TMDDAC
Stage 1 37.45 g (37.45 % w/w) ST
37.45 g (37.45 % w/w) BA
0.1 g (0.1 % w/w) DMEG (75% of the total weight of the monomers)
25 0.167g (0.167 % w/w) azo initiator
Copolymerization: 0.332 g (0.332 % w/w) azo initiator
Stage 2 9.0 g (9 % w/w) ST
9.0 g (9 % w/w) BA
30 7.0 g (7 % w/w) 2-M-5-VP (25% of the total weight of the monomers)

10

0.167 g (0.167 % w/w) azo initiator (added in 2 h after beginning of stage 2)

Monomer feeding rate: 6.25 g/h

Monomer/water ratio: 1:2

5

Example 5

A procedure according to example 1 with the exception that the temperature was finally raised to 80 °C, was performed with the following amounts of starting materials:

10

Seed polymerization: 4.0 g (4 % wt.) TMDDAC

Stage 1 29.98 g (29.98 % w/w) ST

36.62 g (36.62 % w/w) BA

15

0.1g (0.1 % w/w) DMEG (66.7% of the total weight of the monomers)

0.167g (0.167 % w/w) azo initiator

Copolymerization: 0.334 g (0.334 % w/w) azo initiator

Stage 2 11.62 g (11.62 % w/w) ST

20

14.18 g (14.18 % w/w) BA

5.0 g (5 % w/w) 2-M-5-VP

2.5 g (2.5 % w/w) 1,2-DM-5-VP methylsulphate (1,2-dimethyl-5-vinylpyridinium methyl sulphate) (33.3% of the total weight of monomers)

25

0.167 g (0.167 % w/w) azo initiator (added in 2 h after the beginning of stage 2)

Monomer feeding rate: 8,33 g/h

Monomer/water ratio: 1:2

30

Example 6

A procedure was performed according to example 1, with the exceptions that no hydrochloric acid was added in the beginning of the copolymerization stage and the heating time of the latex after completing of stage 2 was 1 h at 70 °C and 2 h at 75 °C, with the following amounts of starting materials:

	Seed polymerization:	2.0 g (2 % w/w) TMDDAC
	Stage 1	22.45 g (22.45 % w/w) ST
10		27.45 g (27.45 % w/w) BA
		0.1 g (0.1 % wt.) DMEG (50% of the total weight of the monomers)
		0.167 g (0.167 % w/w) azo initiator
	Copolymerization	0.167 g (0.167 % w/w) azo initiator
15	Stage 2	18.0 g (18 % w/w) ST
		22.0 g (22 % w/w) BA
		10.0 g (10 % w/w) 2-M-5-VP (50% of the total weight of monomers)
20		0.167 g (0.167 % w/w) azo initiator (added in 2 h after the beginning of stage 2)
		0.167 g (0.167 % w/w) azo initiator (added when monomer feeding of stage 2 is finished)
	Monomer feeding rate:	12,5 g/lh
25	Monomer/water ratio:	1:2

Example 7

A procedure according to example 1 with the exceptions that no hydrochloric acid was added in the beginning of the copolymerization stage, only one portion of azo initiator was added at the end and the heating time of the latex after completing of stage 2 was 1 h at 70 °C and 2 h at 75 °C, was performed with the following amounts of starting materials:

12

	Seed polymerization:	4.0 g (4 % w/w) TMDDAC
	Stage 1	19.1 g (19.1 % w/w) ST
		23.35 g (23.35 % w/w) BA
5		0.1 g (0.1 % w/w) DMEG (42.6% of the total weight of monomers)
		0.167 g (0.167 % w/w) azo initiator
	Copolymerization:	0.501 g (0.501 % w/w) azo initiator
	Stage 2	19.1 g (19.1 % w/w) ST
		23.35 g (23.35 % w/w) BA
10		15.0 g (15 % w/w) 2-M-5-VP (57.4% of the total weight of monomers)
		0.167 g (0.167 % w/w) azo initiator (added in 2 h after the beginning of stage 2)
	Monomer feeding rate:	14,36 g/h
15	Monomer/water ratio:	1:2

Example 8

A procedure according to example 1 with the exceptions that no hydrochloric acid was added in the beginning of the copolymerization stage, the temperature was finally raised to 80 °C and the heating time of the latex after completing of stage 2 was 1 h at 70 °C and 2 h at 80 °C, was performed with the following amounts of starting materials:

25	Seed polymerization:	4.0 g (4 % w/w) TMDDAC
	Stage 1	11.83 g (11.83 % w/w) ST
		13.07 g (13.07 % w/w) BA
		0.10 g (0.10 % w/w) DMEG (25.0% of the total weight of monomers)
30		0.167 g (0.167 % w/w) azo initiator
	Copolymerization:	0.332 g (0.332 % w/w) azo initiator
	Stage 2	30.87 g (30.87 % w/w) ST

13

34.13 g (34.13 % w/w) BA

5 g (5 % w/w) 2-M-5-VP

5 g (5 % w/w) 1,2-DM-5-VP methylsulphate (75.0% of the total weight of monomers)

5 0.167 g (0.167 % w/w) azo initiator (added in 2 h after the beginning of stage 2)

0.167 g (0.167 % w/w) azo initiator (added when monomer feeding at stage 1 is finished)

Monomer feeding rate: 19.36 g/h

10 Monomer/water ratio: 1:2

Example 9

A procedure according to example 8 with the exceptions that 5 g DEAEMA and
 15 5 g 2-M-5-VP were used as amine monomers, and at the beginning of stage 2
 5.0 ml of 5 % HCl aqueous solution was added to the seed latex. Monomer feeding
 rate at stage 2 was 19.36 g/h and monomer/water ratio is 1:2.

Example 10

20

A procedure according to example 1, with the exceptions that the amount of hydrochloric acid added in the beginning of the copolymerization stage was 5.0 ml and the temperature was finally raised to 80 °C, was performed with the following amounts of starting materials:

25

Seed polymerization: 4.0 g (4.0 % w/w) TMDDAC

Stage 1 11.87 g (11.87 % w/w) ST

13.13 g (13.13 % w/w) BA

30

0.1 g (0.1 % w/w) DMEG (25% of the total weight of monomers)

0.162 g (0.162 % w/w) azo initiator

Copolymerization: 0.333 g (0.333 % w/w) azo initiator

14

Stage 2
28.43 g (28.43 % w/w) ST
31.47 g (31.47 % w/w) BA
7.5 g (7.5 % w/w) DEAEMA
7.5 g (7.5 % w/w) 2-M-5-VP (75% of the total weight
of the monomers)
0.167 g (0.167 % w/w) azo initiator (added in 2 h after
the beginning of stage 2)
0.167 g (0.167 % w/w/w) azo initiator (added when
monomer feeding of stage 2 is finished)
Monomer feeding rate: 18.75 g/h
Monomer/water ratio: 1:2

Example 11

A procedure according to example 8 with the exceptions that 6.5 g DMAEMA and 6 g 2-M-5-VP were used as amine monomers. Monomer feeding rate was 19.36 g/h at stage 2 and monomer/water ratio is 1:2.

Example 12

A procedure according to example 10 with the exceptions that 7.5 g DMAEMA and 7.5 g 2-M-5-VP were used as amine monomers. Monomer feeding rate was 18—75 g/h at stage 2 and monomer/water ratio is 1:2.

Example 13

A procedure according to example 1, by stepwise feeding of TMDDAX (20 % at stage 1, 80 % at stage 2), with the exceptions that the amount of hydrochloric acid added in the beginning of the copolymerization stage was 6.0 ml and temperature was finally raised to 80 °C, was performed with the following amounts of starting materials:

15

	Seed polymerization:	0.8 g (0.8 % w/w) TMDDAC
	Stage 1	11,83 g (11.83 % w/w) ST
		13,07 g (13.07 % w/w) BA
5		0.1 g (0.1 % w/w) DMEG (25% of the total weight of monomers)
		0.167 g (0.167 % w/w) azo initiator
		100 g water
	Copolymerization:	0.333 g (0.333 % w/w) azo initiator
		0,8 g (0.8 % w/w) TMDDAC
10		31.87 g (31.87 % w/w) ST
		33.13 g (33.13 % w/w) BA
		5.0 g (5.0 % w/w) DEAEMA)
		5.8 g (5.0 % w/w) 2-M-5-VP (75% of the total weight of the monomers)
15		0.8 g (0.8 % w/w) TMDDAC is added in 1 h after the beginning of stage 2
		0.8 g (0.8 % w/w) TMDDAC
		0.167 g (0.167 % w/w) azo initiator (added in 2 h after beginning of stage 2)
20		0.8 g (0.8 % w/w) TMDDAC (added in 3 h after the beginning of stage 2)
		0.167 g (0.167 % w/w) azo initiator (added when monomer feeding is finished)
	Monomer feeding rate:	19.36 g/h
25	Monomer/water ratio:	1:1

Example 14

A procedure according to example 13 with 15.0 g DMAEMA as amine monomers
 30 and 140 g water at stage 1 was carried out.

Monomer feeding rate: 19.36 g/h
 Monomer/water ratio: 1:1.4

Example 15

A procedure according to example 13 with 15.0 g DMAEMA as amine monomers.

Monomer feeding rate: 19.36 g/h

5

Monomer/water ratio: 1:1

Comparative examples:**Example 16**

10

200 g deionized water, 2.0 g anionic surfactant E-30 (alkyl C₁₁-C₁₇ sodium sulphate) and 2.0 g non-nonionic surfactant OS-20 (C16-C18 oxy-ethylated alcohol) are charged into the reactor. The reaction mixture is heated to 80 °C, the emulsifiers are dissolved. Then the monomer mixture consisting of 3.2 g ST, 2.14 g BA and
15 1.33 g DEAEMA amounting to 6.67 % of the total weight of comonomers, is charged, and 0.2 g tertiary dodecyl mercaptane (T-DDM) as chain-transfer agent and 1.0 g potassium persulphate are added. Seed copolymerization is carried out at 80°C for 0.5 h. Then the monomer mixture consisting of 12.8 g ST, 8.56 g BA and 5.34 DEAEMA amounting to 26.66 % of the total weight of comonomers is fed into the
20 seed latex as well as 0.8 g T-DDM at 80 °C for 0.5 h with the feeding rate of 55 g/h. During the feeding of the monomer mixture the temperature of the seed latex is maintained at 80 °C for 1 h. Then the amine groups of the seed latex are neutralized by feeding 11.6 ml 5 % HCl aqueous solution to the latex at 80 °C for 0.5 h. As a result of the neutralization 75% of the amine groups of the copolymer are
25 transferred to ionized form. At stage 2, 0.5 g potassium persulphate is added to the seed latex and the monomer mixture is fed at 80 °C for 1 h with the feeding rate of 66.7 g/h. The mixture consists of 33.33 g ST and 33.3 g BA amounting to 66.7 % of the total weight of comonomers. The latex is maintained at 80 °C for 1 h, the remaining 25 % of the amine groups of the copolymer are neutralized with 4.0 ml
30 of 5 % HCl aqueous solution which is added to the latex during 0.5 h. Then the latex is maintained at 80 °C for 0.5 h, cooled and collected. The monomer/water ratio is 1:2.

Example 17

200 g deionized water, 0.167 g (0.167 % w/w) TMDDAC are charged into the reactor, the reaction mixture is heated to 80 °C, the emulsifier is dissolved and the
5 reaction mixture consisting of 3.2 g (3.2 % w/w) ST, 2.13 g (2.13 % w/w) BA and 1.33 g (1.33 % w/w) DEAEMA amounting to 6.66% of the total weight of copolymers, 0.2 g (0.2 % w/w) chain transfer agent (T-DDM), 1.0 g (1 % w/w) 2,2'-azo-bis (2-amine propane) dihydrochloride is charged and seed copolymerization is carried out for 0.5 hr at 80 °C. Then for 0.5 h the monomer mixture consisting of
10 12.8 g (12.8 % w/w) ST, 8.54 g (8.54 % w/w) BA and 5.34 g (5.34 % w/w) DEAEMA amounting to 26.68 % of the total weight of comonomers and 0.8 g (0.8 % w/w) T-DDM is fed into the reaction mixture with the rate of 54.96 g/h. When the feeding of the monomers is finished the reaction mixture is kept at 80 °C for 1 h. When stage I is finished the latex is neutralized with 11.6 ml of 5% aqueous
15 solution of hydrochloric acid during 0.5 h. As a result of neutralization 75% of the amine groups are transformed into ionized form. In stage 2 0.5 g (0.5 % w/w) azo initiator is fed into the latex and the monomer mixture consisting of 33.33 g (33.33 % w/w) ST, 13.33 g (13.33 % w/w) BA and 20 g (20 % w/w) butyl methacrylate (BMA) amounting to 66.66 % of the total weight of comonomers, is
20 charged for 1 h with the rate of 66.7 g/h. The latex is kept at 80 °C for 1 h. When stage 2 is finished 25 % of the amine groups are neutralized with 3.9 ml of 5 % aqueous solution HCl for 0.5 h. The obtained latex is kept at 80 °C for 0.5 h, cooled and collected. The monomer/water ratio is 1:2.

Properties of latexes and polymeric coatings obtained in Examples 1—17

No. Example	Properties of polymeric coating					
	Water absorption (%/day)	Surface resistivity/RH (ohm) (%)	Tensile strength (MPa)	Elongation at break (%)	Peel resistance (kN/m)	Relative hardness
1	19.5	$1.0 \cdot 10^{11}$ / 58	10.5	490	0.43	0.39
2	24.0	$8 \cdot 10^{11}$ / 63	11.2	440	0.41	0.70
3	5.4	$8 \cdot 10^{10}$ / 63	16.2	350	0.40	0.65
4	6.7	$1.7 \cdot 10^{10}$ / 63	15.7	380	0.41	0.62
5	24.2	$2.0 \cdot 10^{11}$ / 63	4.7	710	0.32	0.49
6	13.1	$2.4 \cdot 10^{11}$ / 63	15.2	390	0.35	0.76
7	11.7	$3.4 \cdot 10^{11}$ / 63	14.5	380	0.42	0.77
8	21.1	$1.2 \cdot 10^{10}$ / 63	4.2	700	0.36	0.52
9	24.6	$1.1 \cdot 10^{10}$ / 63	12.4	390	0.40	0.42
10	17.2	$6 \cdot 10^8$ / 65	7.1	470	0.35	0.23
11	14.2	$7.0 \cdot 10^9$ / 32	4.2	700	0.36	0.52
12	11.8	$2.9 \cdot 10^9$ / 32	12.4	390	0.42	0.43
13	12.2	$219 \cdot 10^9$ / 60	12.2	410	0.41	0.44
14	15.1	$9.7 \cdot 10^7$ / 60	13.8	210	0.44	0.42
15	14.2	$239 \cdot 10^7$ / 60	13.5	220	0.41	0.43
Comparative Examples						
14	52.7	$1.5 \cdot 10^{15}$ / 63	10.5	410	0.15	0.53
15	130.5	$1.8 \cdot 10^{12}$ / 63	9.5	430	0.40	0.65

Properties of latexes and polymeric coatings obtained in Examples 1—17

Residual monomers (%)										
No. Example	pH	Solid content (% w/w)	Average particle diameter (nm)	Coagulation (%)	DEAEMA	DMAEMA	2-M- <i>n</i> -VP	DMEG	BA	ST
1	4.0	33.8	125		-			-	0.08	0.04
2	4.5	33.6	100				-	-	0.05	0.06
3	6.7	33.2	100	-			<0.001	-	0.12	0.024
4	6.8	33.8	90	-			-	-	0.08	0.006
5	6.2	33.9	100	-			-	-	0.12	<0.001
6	6.6	33.6	155	-			-	-	0.12	0.04
7	7.3	33.5	130	-			0.001	-	0.18	0.05
8	4.2	33.6	150	-			-	-	0.14	0.03
9	4.5	33.2	1700	-	-		-	-	0.21	0.06
10	4.5	32.0	260	3.9	0.001		-	-	0.15	0.07
11	3.9	33.6	165	-	-		-	-	0.10	0.08
12	3.2	33.5	150	-	0.01	0.01	0.01	-	0.15	0.05
13	3.2	51.6	165						0.15	0.03
14	1.2	43.8	195						0.17	0.02
15	1.5	48.1	230	0.2					0.15	0.04
Comparative Examples										
16	4.2	33.1	2500	-	-				0.24	0.08
17	5.0	32.4	1850	-	-				0.05	0.02

Claims

1. A process for the manufacture of antistatic copolymer latexes based on vinyl aromatic compounds, alkyl esters of methacrylic acid or acrylic acid and amine
5 alkyl esters of methacrylic acid and/or vinyl pyridine derivatives, **characterized** in that the latexes of the above copolymers are prepared by emulsion copolymerization in the presence of trimethyl alkyl ammonium halogenide in the amount of 2—4 % of the total weight of the monomers in combination with a water soluble initiator, wherein the formation of latex particles with the direct morphology
10 of core-shell takes place, the core comprising the copolymer formed in stage 1 of the process and the shell comprising the copolymer formed in stage 2 of the process.
2. A process according to claim 1, **characterized** in that copolymer latexes are
15 prepared by seed emulsion copolymerization wherein the seed latex is prepared by copolymerization of vinyl aromatic compound, alkyl ester of methacrylic acid or acrylic acid and dimethacrylic ester of ethylene glycol as a cross-linking agent with the weight ratio of monomers equal to 20-80:79—19.9:1.0—0.1 and the feeding of the monomer mixture to the emulsifier solution is performed in a single
20 step, and the amount of the monomers used for the preparation of the seed latex is equal to 25—75 % of the total amount of monomers.
3. A process according to claims 1 or 2, **characterized** in that stage 2 of the process is carried out by stepwise feeding of vinyl aromatic compound, alkyl ester
25 of methacrylic acid or acrylic acid, amine alkyl ester of methacrylic acid and/or vinyl pyridine derivative with the weight ratio of monomers equal to 25—50:65—15:10-35 or vinyl aromatic compound, alkyl ester of methacrylic acid or acrylic acid, amine alkyl ester of methacrylic acid and/or vinyl pyridine derivative, dimethacrylic ester of ethylene glycol with the weight ratio of monomers
30 equal to 25—50:64—14.9:10—35:1.0—0.1 seed latex.
4. A process according to any of claims 1—3, **characterized** in that the initiator is fed to the reaction mixture in the amount of 0.4—1.0 % of the total weight of monomers, stepwise during latex copolymerization.

5. A process according to any of claims 1—4, **characterized** in that the initiator is 2,2'-azo-bis-(2-aminepropane) dihydrochloride.
6. A process according to any of claims 1—5, **characterized** in that latex
5 copolymerization is carried out at pH of the reaction medium equal to 1-8.
7. Process according to any of claims 1—6, **characterized** in that the cationic surfactant is added to the reaction mixture at the first stage of the process or it is added stepwise during stages 1 and 2.
10
8. Process according to any of claims 1—7, **characterized** in that the cationic surfactant is cetyl, dodecyl or stearyl trimethylammonium halogenide.
9. Process according to any of claims 1—8, **characterized** in that the cationic
15 surfactant is dodecyl trimethylammonium halogenide.
10. Process according to any of claims 1—7, **characterized** in that the seed latex is prepared by copolymerization of vinyl aromatic compound, alkyl ester of methacrylic acid or acrylic acid and dimethacrylic ester of ethylene glycol as a
20 cross-linking agent with the weight ratio of monomers equal to 40—60:59.8—39.6:0.2—0.4.
11. Process according to any of claims 1—8, **characterized** in that that stage 2 of the process is carried out by stepwise feeding of vinyl aromatic compound, alkyl
25 ester of methacrylic acid or acrylic acid, amine alkyl ester of methacrylic acid and/or vinyl pyridine derivative with the weight ratio of monomers equal to 33—40:53—22:14—28 or alternatively with feeding of vinylaromatic compound, alkylester of methacrylic acid or acrylic acid, aminealkyl ester of methacrylic acid and/or vinylpyridine derivative, dimethacrylic ester of ethylenelycol as a cross-
30 linking agent with the weight ratio of monomers equal to 36.3—51.6:54—34:9.5—14:0.2—0.4.
12. An antistatic latex composition, **characterized** in that it comprises antistatic latex copolymer manufactured according to any of claims 1—9.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/FI 98/00480

A. CLASSIFICATION OF SUBJECT MATTER

IPC6: C08F 257/02, C08F 265/04

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC6: C08F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

SE,DK,FI,NO classes as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

WPI

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	STN International, File CAPLUS, CAPLUS accession no. 1992:22419, Asahi Chemical Industry Co., Ltd: "Cationic hollow polymer particles, their preparation, and paper containing them", JP,A2,03074440, 910329, Heisei	1-12
	--	
A	EP 0414351 A1 (IMPERIAL CHEMICAL INDUSTRIES PLC), 27 February 1991 (27.02.91), page 4, line 29 - line 30; page 6, line 7 - line 42, abstract, example 5	1-12
	--	
A	EP 0573783 A1 (SUMITOMO CHEMICAL COMPANY, LIMITED), 15 December 1993 (15.12.93), abstract	1-12
	--	

☒ Further documents are listed in the continuation of Box C.☒ See patent family annex.

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Date of the actual completion of the international search

10 Sept. 1998

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11 -09- 1998

Name and mailing address of the ISA/
 Swedish Patent Office
 Box 5055, S-102 42 STOCKHOLM
 Facsimile No. +46 8 666 02 86

Authorized officer

Barbro Nilsson
 Telephone No. +46 8 782 25 00

INTERNATIONAL SEARCH REPORT

International application No.

PCT/FI 98/00480

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p>File WPI, Derwent accession no. 81-48863D, Matsushita Elec Ind Co Ltd: "Antistatic compsn. for plastics - comprises epoxy cpd. -acrylic acid reaction product, N-vinyl pyrrolidone, hydroxyalkyl (meth)acrylate, quat. ammonium cpd. and initiator;" & JP,A,56057870, 810520, DW8127</p> <p>--</p>	1-12
A	<p>US 5604076 A (RAJ D. PATEL ET AL), 18 February 1997 (18.02.97), abstract</p> <p>-- -----</p>	1-12

INTERNATIONAL SEARCH REPORT
Information on patent family members

27/07/98

International application No.
PCT/FI 98/00480

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 0414351 A1	27/02/91	AT 117704 T	15/02/95
		AU 638472 B	01/07/93
		AU 5979690 A	31/01/91
		CA 2020844 A	26/01/91
		DE 69016306 D,T	24/05/95
		IE 66822 B	07/02/96
		JP 2505062 B	05/06/96
		JP 3101829 A	26/04/91
		PT 94796 A	20/03/91
		US 5210113 A	11/05/93
		US 5296524 A	22/03/94
EP 0573783 A1	15/12/93	JP 6016742 A	25/01/94
		US 5306776 A	26/04/94
		US 5424370 A	13/06/95
		JP 6049150 A	22/02/94
US 5604076 A	18/02/97	NONE	